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(54) Title: HEAT ACTIVATED EPOXY ADHESIVE AND USE IN A STRUCTURAL FOAM INSERT

(57) Abstract: An expandable adhesive for a structural foam insert useful for vehicular reinforcement is described. The adhesive is characterized by containing a viscosity enhancing agent such as a polymethylmethacrylate, which results in a cured adhesive having unusually small voids and unusually high Young's modulus.

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HEAT ACTIVATED EPOXY ADHESIVE AND USE IN A STRUCTURAL FOAM INSERT

The present invention relates to a heat activated epoxy adhesive and its use in a foam insert that is bonded to a metal body. Structural foam inserts (SFIs) have been developed to reinforce structures within motor vehicles to add strength and stiffness to the vehicle at the site of insertion. Acoustical foam inserts (AFI) have been developed to reduce the impact of noise and vibration on vehicle passages. For example, an SFI coated with an uncured expandable epoxy adhesive is secured to the B-pillar cavity of an automobile. An AFI is typically placed in a hollow part of an automobile for the purpose of preventing the transmission of noise and vibration throughout the hollow cavity. AFI may comprise a foam coated with an expandable adhesive. The automobile body is then subjected to electrodeposition coating (e-coating) and bake, whereupon the epoxy adhesive expands through heat activation to form a bond between the foam insert and the sheet metal. However, one problem associated with expandable adhesives of the prior art is their propensity to crosslink before they expand. This premature crosslinking results in ineffective wet-out of the vehicular substrate and concomitant weaker bonding. Furthermore, solving the problem of premature crosslinking – for example, by reducing or eliminating catalyst – creates another problem, namely, the formation of a cured expanded polymer with acceptable adhesion at the expense of large voids (number weighted mean diameter of > 2000 μm), the formation of which decreases durability and results in reduction in mechanical properties.

It would therefore be an advance in the art of foam inserts to provide an expandable adhesive for the insert that efficiently wets out a substrate before crosslinking occurs, thereby creating optimal chemical bonding and enhanced durability, but which produces small voids, thereby resulting in enhanced mechanical properties.

The adhesive of the present invention can expand up to 350 percent. To insure the cavity is filled, expansion is limited by the available space in the cavity. The adhesive present invention creates an equalizing pressure which helps align the part in the cavity.

The present invention addresses a need in the art by providing an expandable adhesive comprising a) a cured 1-part epoxy resin; b) a viscosity increasing agent; and c) not greater than 25 parts by weight of an inorganic filler, based on 100 parts of the epoxy resin, wherein the adhesive when expanded contains voids having a number average or weighted mean diameter of less than 1000 μm.

In a second aspect, the invention is a structural foam insert comprising a) an expanded polymer, and b) an expandable adhesive contacting the expanded polymer, which expandable adhesive contains i) a 1-part epoxy resin; ii) a polymeric viscosity enhancing agent; iii) a blowing agent; iv) a catalyst; and v) a curing agent, wherein the expandable adhesive has a Young's modulus of at least 500 mPa at 100 percent expansion, preferably 600 mPa at 150 percent expansion.

In a third aspect, the present invention is a reinforced vehicular frame comprising a) an expanded polymer, and b) an expanded adhesive bonding the expanded polymer and the vehicular frame, which expanded adhesive contains i) 1-part cured epoxy resin; and ii) a polymeric viscosity enhancing agent; wherein the expanded adhesive has a Young's modulus of at least 500 mPa at 100 percent expansion.

In a fourth aspect, the present invention is a method of preparing foam insert comprising the steps of 1) contacting an expandable adhesive with an expanded polymer under conditions sufficient to gel the expandable adhesive without crosslinking; b) placing the expanded polymer with the gelled expandable adhesive within a vehicular frame; c) heat activating the expandable adhesive to create a expanded adhesive that forms a bond between the expanded polymer and the vehicular frame; d) curing the expanded adhesive; wherein the expandable adhesive contains i) a 1-part epoxy resin; ii) a polymeric viscosity enhancing agent; iii) a blowing agent; iv) a catalyst; and v) a curing agent, and wherein the expanded adhesive contains voids having a number weighted mean diameter of < 1000 μm.

In a fifth aspect, the present invention is an expanded adhesive comprising a) a cured 1-part epoxy resin; b) a viscosity increasing agent; and c) not greater than 25 parts by

weight of an inorganic filler, based on 100 parts of the epoxy resin, wherein the expanded adhesive contains voids having a number weighted mean diameter of <1000 μm.

The present invention addresses a problem in the art by providing an foam insert with an adhesive that efficiently wets out a substrate before crosslinking occurs, thereby creating superior chemical bonding and enhanced durability, but which produces reduced cell structure, thereby resulting in enhanced mechanical properties. The adhesive of the present invention can expand up to 350 percent. To insure the cavity is filled, expansion is limited by the available space in the cavity. The adhesiveof the present invention creates an equalizing pressure which helps align the part in the cavity.

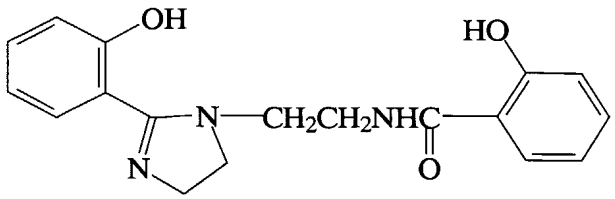
The expanded polymer (also known as a rigid foam) used to make the foam insert has a Young's modulus of preferably at least 200 mPa, more preferably at least 350 mPa; a T_g of preferably at least 50°C, and more preferably at least 80°C; and a density of less 1 g/cm^3, more preferably less than 0.7 g/cm^3 and preferably at least 0.0016 g/cm^3 and more preferably at least 0.08 g/cm^3, even more preferably at least 0.3 g/cm^3. The expanded polymer can be any expanded polymer with dimensional stability when expanded and which provides structural integrity or acoustical sealing properties. Preferred examples of expanded polymers include expanded polyurethane, expanded polystyrene, expanded polyolefin, and expanded 2-part epoxy. A more preferred expanded polymer is an expanded polyurethane. The dimension of the expanded polymer is designed to be 3-6 mm smaller in each dimension than the size of the cavity to which it is to be inserted.

The one part adhesive comprises any one part adhesives which expands and bonds to the expanded foam and the material from which the interior of the vehicle cavity is made. The expandable adhesive that is used to coat the expandable polymer is prepared using a 1-part epoxy resin formulation. Preferred epoxy resins include diglycidyl ethers of bisphenol A and bisphenol F, as well as oligomers of diglycidyl ethers of bisphenol A and bisphenol F, either alone or in combination. More preferably, the epoxy resin is a mixture of diglycidyl ether of bisphenol A and an oligomer of diglycidyl ether of bisphenol A. The

epoxy resin preferably constitutes from 40 weight percent to 80 weight percent of the total materials used to make the expandable adhesive.

The polymeric viscosity increasing agent is a polymer that increases the viscosity of the blend used to make the expandable adhesive to control the release and coalescence of gases produced by the blowing agent. The viscosity increasing agent is preferably used as a fine powder (volume mean average <200 μm) and preferably has a T_g of at least 70°C, more preferably at least 100°C. Examples of polymeric viscosity increasing agents include polyvinyl butyrates; phenoxy resins, polystyrene, polycarbonates and polymeric acrylates and methacrylates and polyvinyl formal. Examples of more preferred polymeric viscosity increasing agents include polymeric acrylates and methacrylates, more preferably polymethylmethacrylate (PMMA), most preferably a carboxylic acid functionalized PMMA such as the commercially available Degalan™ 4944F PMMA (available from Rohm America). The polymeric viscosity increasing agent is used in an effective amount to control release of gas from the blowing agent so as to reduce cell size in the resultant cured resin. The concentration of the polymeric viscosity increasing agent is preferably at least 2, more preferably at least 5, and most preferably at least 10 weight percent; and preferably not more than 40 weight percent, more preferably not more than 30 weight percent, and most preferably not more than 20 weight percent, based on the total materials used to make the expandable adhesive.

The polymerization of the epoxy resin is catalyzed by an effective amount of a polymerizing promoting catalyst, preferably from 0.1 weight percent to 2 weight percent, based on the total materials used to make the expandable adhesive. Suitable catalysts include, but are not restricted to, ureas and imidazoles. An example of a preferred catalyst is Acclerine CEL 2191 (1-(2-(2-hydroxbenzamido)ethyl)-2-(2-hydroxyphenyl-2-imidazoline, which has the following chemical structure:



The preparation of this catalyst is described by Bagga in U.S. Patent 4,997,951, which description is incorporated herein by reference.

The epoxy resin is expanded to a desired volume in the presence of an effective amount of a blowing agent to achieve the desired foam structure and density, preferably from 0.5 weight percent to 10 weight percent, more preferably from 0.5 to 3 weigh percent, and most preferably from 1 to 2 weight percent, based on the total materials used to make the expandable adhesive. Preferred blowing agents are heat activatable at least 100°C, more preferably at least 120°C; and preferably not greater than 160°C. Examples of suitable blowing agents include those described by Fukui in U.S. 6,040,350, column 4, lines 25-30, which section is incorporated herein by reference. An example of a preferred commercially available blowing agent is Celogen AZ™ 120 azodicarbonamide (both from Crompton).

The expandable adhesive may further comprise a known rheology control agent such as fumed silica. Surfactants can also be used in the expandable adhesives, such as silane or titanate based surfactants.

The epoxy resin is cured with an effective amount of a curing agent, preferably from 2 to 10 weight percent, based on the total materials used to make the expandable adhesive . Examples of suitable curing agents include those described by Fukui in column 4, line 66-67 and column 5, lines 1-9, which sections are incorporated herein by reference.

Preferred curing agents include dicyandiamide such as AMICURE CG-1200 (from Air Products)..

A sufficient amount of curing agent is used to form the desired foam structure and to provide dimensional stability, preferably 2 or greater of weight percent, even more

preferably 3 weight percent or greater, and most preferably 4 weight percent or greater, and preferably 10 weight percent or less, even more preferably 8 weight percent or less and most preferably 6 weight percent or less.

The expandable adhesive may also include any filler which has a small enough particle size for mixing may be used. The filler may be organic or inorganic. Among preferred organic fillers are polyethylene, polypropylene, polyurethane, rubber and polyvinyl butyral. Among preferred inorganic fillers are calcium carbonate, talc, silica, calcium metasilicate aluminum, hollow glass spheres, and the like. More preferred organic fillers are polyolefin polymeric fillers, such as a polyethylene copolymers. More preferred inorganic fillers include calcium carbonate. The amount of filler is preferably not greater than 25 parts by weight, more preferably not greater than 15 parts by weight, and most preferably not greater than 10 parts by weight, relative to 100 parts by weight of the epoxy resin used to make the expandable adhesive.

A preferred expandable adhesive is prepared by combining and mixing the epoxy resin, the blowing agent, the catalyst, the curing agent, the viscosity increasing agent, and optionally the fillers at a temperature above ambient temperature, preferably from 30°C to 50°C for 15 minutes to 2 hours. Entrapped air is removed *in vacuo* and the expandable adhesive is then injected into a hot mold (100°C to 130°C) that surrounds and conforms to the shape of the expanded polymer to achieve variable designed thicknesses of adhesive over the expanded polymer ranging from 1 mm to 4 mm. The resultant foam insert is affixed within a cavity of an automotive structure so as to create a 1-mm to a 4-mm gap between the foam insert and the metal substrate. The metal structure is then e-coated, with residual e-coat liquid escaping through the gaps between foam insert and the metal. Finally, the e-coat and expandable adhesive are cured at a suitable curing temperature, preferably between 150°C and 200°C.

The preferred cured (expanded) adhesive has a Young's modulus of at least 500 mPa, more preferably at least 700 mPa, and most preferably of at least 1000 mPa at 100 percent expansion. Furthermore, the preferred cured adhesive has surprisingly small voids,

preferably with a number weighted mean diameter of less than 1000 μm, more preferably less than 500 μm, and most preferably less than 100 μm. Consequently, the adhesion of the foam insert to the automotive structure is strong and durable.

The following example is for illustrative purposes only and is not intended to limit the invention in any way. All percentages are weight percent unless otherwise specified.

Example – Preparation of a Structural Foam Insert with Controlled Adhesive Cell Size

A rigid polyurethane foam having a density of 0.64 g/cm^3 and a Young's modulus of 400 mPa was conformed to a desired shape. An expandable adhesive was prepared by adding to a vessel with mixing DER 331 epoxy resin (40 percent), DER 337 epoxy resin (25 percent), CELOGEN AZ 120 blowing agent (1.5 percent), $CaCO_3$ filler (0.45 percent), carbon black (0.9 percent), ACCELERINE CEL 2191 catalyst (1 percent, obtained from Celerity LLC), AMICURE CG1200 dicydiamide, DEGALAN 4944F PMMA (12.1 percent), MICROTHENE FE-532 polyethylene copolymer (10 percent), and CABOSIL TS-720 (4.1 percent) at 40°C for 1 hour. Entrapped air wa then removed by mixing under vacuum for 30 minutes. The blend was injected into a hot mold (120°C) surrounding and conforming to the shape of a polyurethane foam insert so that the expandable adhesive substantially covers the insert to achieve variable designed thicknesses ranging from 2-3 mm for designed variances in final mechanical properties of the expanded adhesive. The adhesive resided in the hot mold for 4 minutes, after which the mold wa cooled to room temperature over a 10-minute period and removed. The resultant FOAM INSERT was affixed within the cavity of an automotive structure to create a 2-mm gap between the SFI and the metal substrate. The metal structure was e-coated at ambient temperatures, with the residual liquid running through the gaps between the SFI and the metal. The structure was heated in an oven for 40 minutes at 180°C to cure the e-coat and to expand and cure the adhesive. The cured adhesive had a Young's modulus of 1033 mPa at 100 percent expansion.

WHAT IS CLAIMED IS:

1. An expandable adhesive comprising a) a cured 1-part epoxy resin; b) a viscosity increasing agent; and c) not greater than 25 parts by weight of an inorganic filler, based on 100 parts of the epoxy resin, wherein the adhesive when expanded contains voids having a number weighed mean diameter of less than 1000 μm.

2. An expandable adhesive according to Claim 1 wherein the polymeric viscosity enhancing agent is a polymethylmethacrylate powder.

3. An expandable adhesive of Claim 1 or 2 wherein the viscosity increasing agent is a carboxylic acid functionalized polymethylmethacrylate.

4. An expandable adhesive of any one of Claims 1 to 3 which contains not greater than 15 parts by weight of an inorganic filler, based on 100 parts of the epoxy resin.

5. An expanded adhesive which comprises an adhesive according to Claim 1 to 4 which is expanded.

6. The expanded adhesive of Claim 5 wherein the voids have a number weighted mean diameter of less than 500 μm.

7. The expanded adhesive of Claims 5 or 6 which has a Young's modulus at 100 percent expansion of at least 1000 mPa.

8. A foam insert comprising a) an expanded polymer, and b) an expandable adhesive contacting the expanded polymer, which expandable adhesive according to any one of Claims 1 to 4.

9. The foam insert of Claim 8 wherein the expanded polymer is a rigid polyurethane foam.

10. A reinforced vehicular frame comprising a) an expanded polymer, and b) an expanded adhesive according to any one of Claims 4 to 6.

11. A method of preparing structural foam insert comprising the steps of a) contacting an expandable adhesive according to any one of Claims 1 to 4 with an expanded polymer under conditions sufficient to gel the expandable adhesive without crosslinking; b) placing the expanded polymer with the gelled expandable adhesive within a vehicular frame; c) heat activating the expandable adhesive to create an expanded adhesive that forms a bond between the expanded polymer and the vehicular frame and d) curing the expanded adhesive.

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Ir ional Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08J9/00 C09J163/00 C08L63/00 C08J9/22 C08J9/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08J C09J C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	DE 101 63 253 A (HENKEL TEROSON GMBH) 10 July 2003 (2003-07-10) examples 1,3-5 paragraphs '0016! - '0018!, '0038! - '0040!	1,5-7
A	WO 02/31077 A (HENKEL CORP ; KOSHY VETTITHARA C (US)) 18 April 2002 (2002-04-18) page 1, lines 5-12 page 2, lines 20-33 page 3, lines 26,27 page 16, lines 16-31; examples	1-11
A	WO 02/088214 A (HENKEL CORP ; AGARWAL RAJAT K (US)) 7 November 2002 (2002-11-07) page 1, lines 5-9 examples	1-11

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 01/41950 A (L & L PRODUCTS INC) 14 June 2001 (2001-06-14) page 2, lines 19-22 page 5, lines 3-17 page 8, lines 19-22	1-11

Form PCT/ISA/210 (continuation of second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

Information on patent family members

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